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CERAMIC PIGMENTS WITH THE MULLITE STRUCTURE BASED ON TOPAZ AND KAOLINITE

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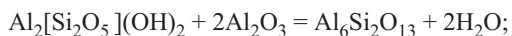
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The possibility of obtaining ceramic pigments with the mullite structure based on natural minerals (kaolinite and topaz) is considered. It is established that these minerals are promising for the synthesis of ceramic pigments. The obtained pigments are resistant to high temperatures and have various tints.

The concepts of synthesis and classification of ceramic pigments keep evolving. A new approach has been taken in the field of raw materials. The current trends imply using less expensive materials: industrial waste and natural minerals. Natural calcium-magnesium silicates and aluminosilicates are the most available and accessible raw materials for ceramic production. Numerous studies [1, 2] are dedicated to the production of ceramic pigments based on natural silicates: diopside, wollastonite, kaolin, etc.

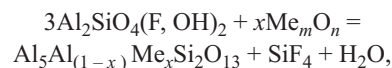
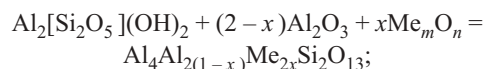
The present study considers the possibility of synthesis of pigments with the mullite structure on the basis of natural minerals (kaolinite and topaz). Ceramic pigments with the mullite structure obtained from pure oxides are sufficiently well studied [3]. The synthesis proceeds at high temperatures and involves a substantial consumption of electricity.

The crystalline structure of topaz and kaolinite transforms into a mullite structure under heat treatment. For complete implementation of the reaction, it is necessary to add Al_2O_3 to kaolinite. The majority of mullite is formed at a temperature of 1200°C; its further increase to 1350°C eliminates the lattice defects and leads to the growth of crystals [4]. As pure topaz is heated, volatile components SiF_4 and H_2O are formed starting at temperatures of 850–900°C; as a consequence, substantial weight losses are observed [5]:



The emergence of the chromophore phase occurs due to the incorporation of the colorant ions into the crystalline structure of the mineral. A transformation of the crystalline lattice

during mullitizing facilitates a fuller incorporation of the chromophore ions:



where $x = 0.1, 0.3, 0.5, 0.7$, and 1.0 mole.

We used topaz concentrate from the Kopna deposit with a main mineral content equal to 90.3% and kaolin from the Prosyantovskoe deposit. The chemical compositions of the materials are listed in Table 1.

The colorant agents in the pigments considered were compounds of transition d -elements: Fe^{3+} , Mn^{2+} , Cr^{3+} , and Co^{2+} . The colorant ions were introduced in the form of soluble salts into a finely milled mineral (topaz, kaolinite) in the amount of 1.5–30 wt.%. The mixture was dried and fired at 1100–1300°C. The compositions of initial batch mixtures with the chromophore additives converted to oxides for some pigments are listed in Table 2.

The obtained pigments were used for underglaze decoration of majolica articles that were fired at 1050°C. The color

TABLE 1

Material	Mass content, %						calcination loss
	SiO_2	Al_2O_3	CaO	MgO	TiO_2	Fe_2O_3	
Topaz concentrate*	35.89	48.19	0.13	0.10	0.19	0.39	15.11
Kaolin**	46.73	37.43	0.71	0.65	0.47	0.72	13.12

* Calcination at a temperature of 1350°C.

** Including also 0.06% K_2O and 0.12% Na_2O .

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TABLE 2

Pigment	Mass content, %						
	kaolin	topaz concentrate	Al ₂ O ₃	CoO	Cr ₂ O ₃	Fe ₂ O ₃	MnO
<i>Pigments based on kaolinite</i>							
BT1*	55.80	—	44.20	—	—	—	—
K1	57.60	—	34.10	8.30	—	—	—
K2	59.30	—	23.40	17.30	—	—	—
K3	52.99	—	31.42	—	15.61	—	—
K4	50.39	—	19.92	—	29.69	—	—
K5	52.55	—	31.16	—	—	16.29	—
K6	49.62	—	19.61	—	—	30.77	—
K7	57.78	—	34.27	—	—	—	7.90
K8	59.90	—	23.70	—	—	—	16.40
<i>Pigments based on topaz</i>							
BT2	—	100	—	—	—	—	—
T1	—	85	—	15	—	—	—
T2	—	80	—	20	—	—	—
T3	—	85	—	—	15	—	—
T4	—	80	—	—	20	—	—
T5	—	85	—	—	—	15	—
T6	—	80	—	—	—	20	—
T7	—	85	—	—	—	—	15
T8	—	80	—	—	—	—	20

* BT) blank test without chromophore additives.

range of the synthesized pigments is wide enough (Table 3). They are light blue and blue shades, as well as green, red, and dark brown. A visual inspection indicates that pigments based on kaolinite have a brighter coloring than pigments based on topaz. First, the crystalline structure of kaolinite probably undergoes a more radical transformation in firing than the topaz structure; therefore, the colorant ions are more fully incorporated. Second, it is supposed that the volatile components under thermal decomposition of topaz entrap and partly carry with them the colorant ions.

An x-ray phase analysis carried out using a DRON-3M diffractometer confirmed that the structure of mullite and kaolinite transforms into a mullite structure. Pigments based on kaolinite contain Al₂O₃ and SiO₂ in the form of corundum and cristobalite, respectively, apart from mullite. A spinel CoAl₂O₄ ($d = 0.143, 0.244, 0.286$ nm) is identified in cobalt pigments with the CoO mass content equal to 8.3% and more. When the ferric oxide Fe₂O₃ content is 16.29% or more, it is registered as an individual phase ($d = 0.368, 0.269, 0.251$ nm), whereas Cr₂O₃ and MnO are not identified, which indicates that the colorant ions are fully incorporated in the mineral lattice. Additives of iron and chromium oxides make the mullite structure more defective; the intensity of the main diffraction peaks decreases (Fig. 1, *a* and *b*).

In topaz pigments, the introduced chromophores are not registered as individual phases. With a CoO content over 15%, the presence of spinel is registered. It is established that the colorant ions have a mineralizing effect on the formation of the mullite structure. The intensity of the diffraction peaks significantly increases compared with the blank test (Fig. 1, *c*

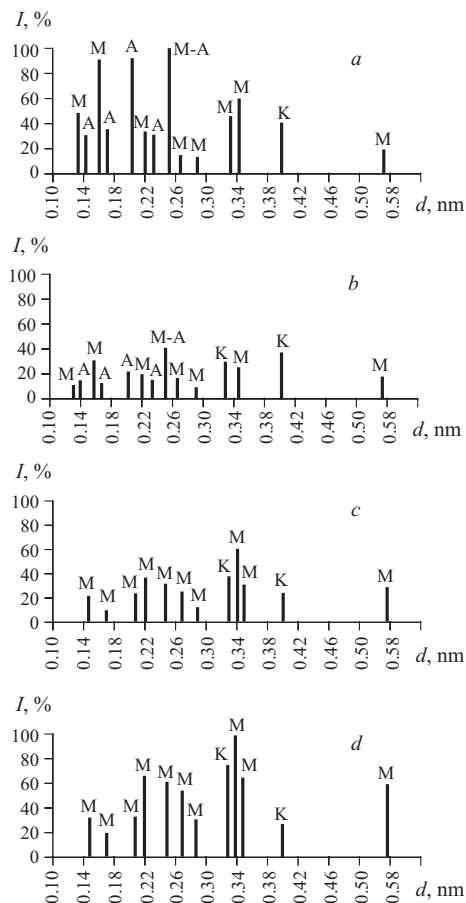


Fig. 1. Strich patterns of blank tests (*a*, *c*) and pigments T3 and K4 (*b*, *d*): M) mullite; K) cristobalite; A) corundum.

and *d*), Such facts are usually observed under low concentrations of the chromophores [6].

The x-ray phase analysis data suggest as well that in firing of topaz-based pigments, the chromophore ions are partly

TABLE 3

Pigment	Color of pigments at firing temperature of 1200°C	Color of underglaze pigments at firing temperature of 1030°C
K1	Light blue	Blue
K2	Blue	Dark blue
K3	Grayish-green	Grayish-green
K4	Glass-green	Dark green
K5	Light coffee	Brown
K6	Chocolate brown	Dark brown
K7	Light brown	Peach
K8	Brown	Brown
T1	Sky-blue	Grayish-sky-blue
T2	Dark blue	Blue
T3	Gray	Grayish-green
T4	Grayish-green	The same
T5	Beige	Sand-colored
T6	Brown	Brown
T7	The same	Coffee
T8	Dark brown	Brown

TABLE 4

Pigment	Color coordinates		Wavelength, nm	Tone purity, %
	x	y		
K2	0.20	0.17	470	25
K4	0.46	0.42	583	71
K6	0.50	0.39	592	72
T1	0.22	0.18	470	12
T4	0.36	0.39	570	34
T5	0.41	0.36	595	56

removed from the mixtures in the form of volatile fluorides. This is confirmed by the chemical analysis data. Depending on the initial concentration and the type of chromophore, up to half of the colorant ions evaporate from the mixture. The remaining chromophores incorporate into the mullite structure and determine the pigment tinting.

An analysis of the pigments was carried out using an SF-18 spectrophotometer to obtain their color characteristics (Table 4).

The studies indicated that natural minerals, such as kaolinite and topaz, are promising materials for producing ceramic pigments. These minerals can be used to synthesize a wide color spectrum of pigments resistant to high temperatures and the aggressive effect of melted glazes. At the same time one should bear in mind the specifics of the reaction of topaz with the chromophores related to the formation of volatile fluorine-bearing components.

Topaz can be used as a material for ceramic pigments individually or mixed with other components in transition to other crystalline structures. Using calcium and magnesium additives, it is possible to produce topaz-based pigments with the structures of anorthite and cordierite, respectively. In this case the intensity of pigment tinting should increase due to

the fact that under a cardinal rearrangement of the crystalline lattice, a higher quantity of the chromophore ions can be incorporated into the mineral structure.

It should be noted that the use of natural materials instead of costly chemicals and a decreased temperature of the pigment synthesis make this technology more cost effective.

Ceramic pigments can be produced from topaz rocks with a topaz content of at least 70%, as well as from quartz-topaz rocks with a lower content of the mineral subjected to concentration. The topaz concentrate is a product of flotation concentration of quartz-topaz waste generated in processing gold-containing ores; therefore, its use as a basis for the synthesis of ceramic pigments partly solves the problem of a complex utilization of raw materials.

The obtained pigments can be used in the production of underglaze or overglaze ceramic paints, as well as in tinting of ceramic mixtures and glazes.

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